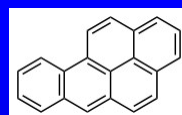


## Basics of Crude Oil



EPA Region 10  
Emergency Management Program  
Spring 2013 OSC Training



## Basics of Crude Oil

- Crude Oil - very complex mixture of hundreds, even thousands of chemical compounds
- Chemical composition can vary tremendously
  - From different producing regions
  - Possible even within a particular formation

## Basics of Crude Oil

- Hydrocarbons are most abundant compounds in crude oil
  - Carbon (80 – 87%)
  - Hydrogen (10 - 15%)
- Non-hydrocarbon compounds, typically <10%
  - Sulfur (0 -10%)
  - Nitrogen (0 – 1%)
  - Oxygen (0 - 5%)
  - Trace Metals
    - V, Ni, Fe, Al, Na, Ca, Cu, U

## Basics of Crude Oil

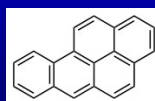
### Classes of Hydrocarbons

- Three classes of compounds
  - Alkanes, or Aliphatics, or Paraffins
  - Cycloalkanes or Cycloparaffins or Napthenes
  - Aromatics
- Paraffins or Aliphatics (Alkanes)
  - Carbon atoms bound to all Hydrogen atoms, fully “saturated”; stable, less reactive than others
  - Methane, ethane, propane, butane, pentane

## Basics of Crude Oil

### Classes of Hydrocarbons

- Napthenes or Cycloalkanes (Cycloparaffins)
  - Saturated hydrocarbons arranged in rings
  - Cyclopropane, cyclobutane, cyclopentane
- Aromatics (Mononuclear & Polynuclear)
  - Contain at least one or more benzene rings
  - Those with 2 or more are PNAs or PAHs
  - Benzene, naphthalene, benzo[a]pyrene,



benzo[a]pyrene

## Basics of Crude Oil

### Non-hydrocarbon Constituents

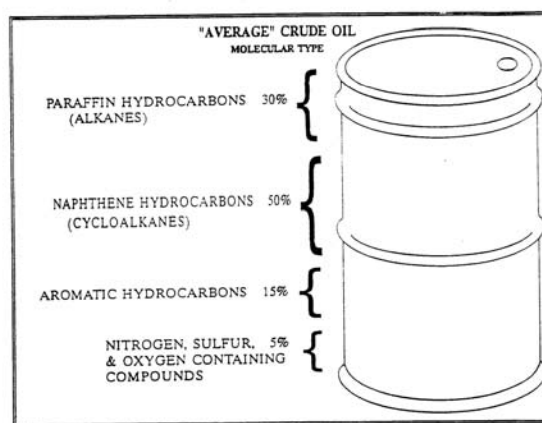
- Sulfur Compounds
  - Very important non-hydrocarbon compounds
  - Hydrogen sulfide, mercaptans, sulfonic acids
- Nitrogen Compounds
  - Present in all crude oils
  - Pyridines, quinolines, pyrroles, etc.
- Oxygen compounds (found in distillation fractions)
  - Organic acids, Alcohols, ketones, esters, phenols
- Trace Metals - V, Ni, Fe, Al, Na, Ca, Cu, U

## Basics of Crude Oil

- Average Crude Oil Molecular Type

Paraffin Hydrocarbons	= 30%
Napthene Hydrocarbons	= 50%
Aromatics	= 15%
NSO Compounds	= 5%

## Basics of Crude Oil Constituents



"AVERAGE" CRUDE OIL MOLECULAR TYPE

Source: U.S. EPA manual for "Inland Oil Spills" course

## Basics of Crude Oil Refining Fractions

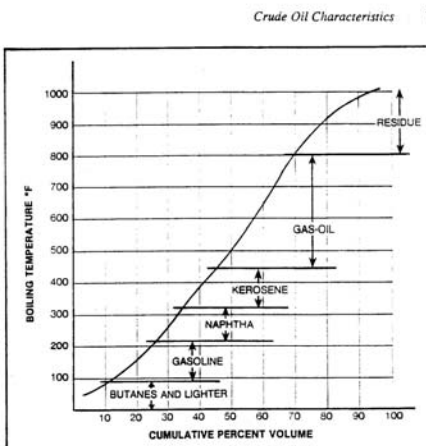


Fig. 2-4 —Crude Oil Distillation Curve and Its Fractions

Source: Petroleum Refining for the Non-Technical Person

## Basics of Crude Oil Refining Fractions

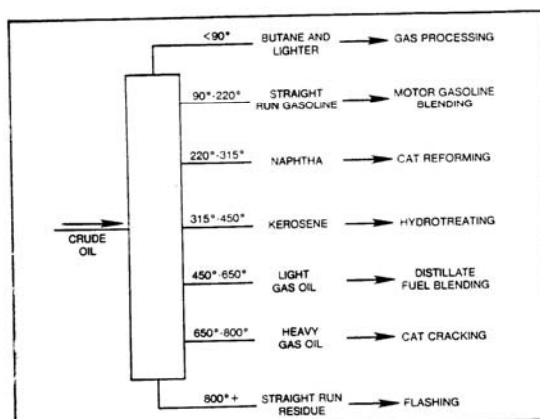


Fig. 3-11 —Distilling Crude and Product Disposition

Source: Petroleum Refining for the Non-Technical Person

## Basics of Crude Oil

### Terminology

- Light Crudes - have more “light ends”, such as gasoline, naphtha, and kerosine fractions
- Heavy Crudes have more heavy ends such as asphaltenes (higher molecular weight)
- Sweet, Sour Crudes: refer to amount of sulfur present
  - Sweet < 0.5% sulfur compounds
  - Sour < 2.5 % sulfur compounds

## Basics of Crude Oil

### Terminology

- API Gravity – a specific scale, created by API, for measuring the relative density of petroleum liquids, expressed in degrees.
  - $\text{API Gravity} = (141.5 / \text{Sp.Gr at } 60^\circ \text{ F}) - 131.5$
- Rule of Thumb
  - Higher API Gravity = lighter the crude, less viscous, more light ends
  - Heavy Crudes ~ API 18°
  - Light Crudes ~ API 36° and above

## Basics of Crude Oil

What does this mean for Oil Spill Response?

- Speaking with same knowledge of terminology
- Different types of crudes (and refined products) have differing fate and transport when spilled
  - Heavy vs light, API Gravity?
- Types of crudes important for Health & Safety, e.g. Sour oil will have H<sub>2</sub>S present
  - Air monitoring at spill, what to look for at production site, etc.

## Basics of Crude Oil

- Examples of 40 Different grades of Crude flow thru the U.S.

<u>Type</u>	<u>API</u>	<u>S%</u>	<u>Type</u>	<u>API</u>	<u>S%</u>
W.T. Sour	33.5	1.78	Bacquero	22.8	1.95
Dom. Sweet	40.0	0.420	Basra	33.5	2.10
ANS	26.4		Kirkuk	33.7	2.14
Bonny Light	35.2	.01750	Brent	38.0	0.3760
Maya	22.5	2.95	Mesa	30.3	0.980
Isthmus	32.5	1.320	Velma	26.4	
Rata	24.2	4.000	Cusian	29.4	0.2950
ABH	27.4	2.700	Olmeca	38.3	0.950



Region 10 Oil Team

## Region 10 Dominant Crude Oils

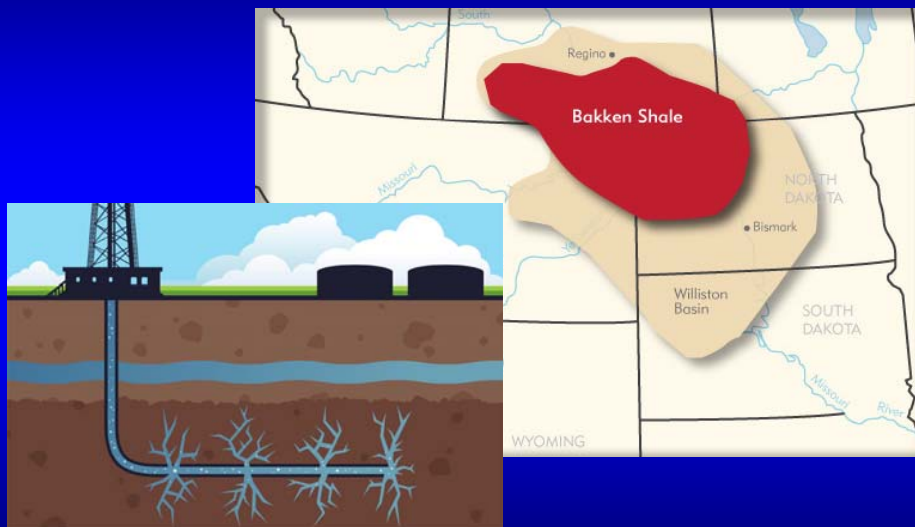
- Alaska North Slope
- Bakken Shale
- Alberta Oil Sands/Tar Sands



## Alaska North Slope



## Bakken Shale



## Bakken Shale Sweet Crude

- Light blend
- API gravity ranging from 40 to 42 degrees
- Sulfur content ranges from 0.17-0.20% (~4000 ppm)
- Generally low in metals content as well as asphaltenes
  - emulsification is relatively low when released to water
- These characteristics allow refiners to process the product rapidly for high throughput

## Region 10 Presence

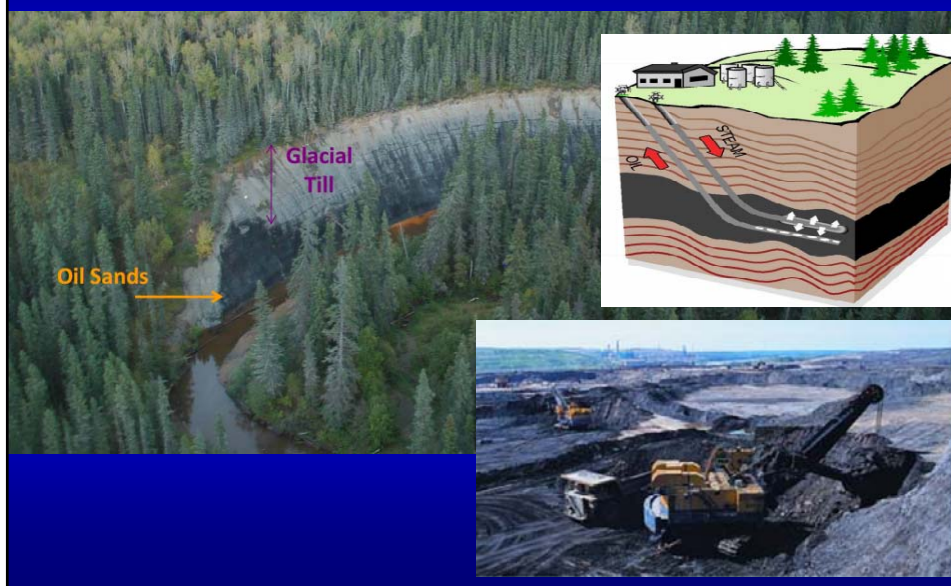
- Tesoro Anacortes - 40,000 bbl/day
- BP Cherry Point - 20,000 bbl/day
- Columbia Pacific Bio-Refinery
  - 67,000 bbl/day
- Tesoro Vancouver – 2014 (120,000 – 280,000 bbl/day)
- Gray's Harbor – under consideration
- Port of Lewiston – under consideration

# Response Considerations

- Properties
- Tactics

cenovus ENERGY		LIGHT CRUDE OIL	
1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION			
Product Identifier	LIGHT CRUDE OIL, Bakken Crude		
Synonyms	Bakken Oil, Bakken Crude		
Chemical Description	A naturally occurring mixture of aromatic hydrocarbons and small amounts of sulfur and nitrogen compounds		
Product Use	Process stream, fuels and lubricants production		
Manufacturer/Supplier	CENOVUS ENERGY INC. 500 Centre Street SE, PO Box 766 Calgary, AB T2P 0M5 Cenovus Energy Inc. Health and Safety 1-403-766-2000 Emergency Telephone: 1-877-458-8080, CANUTEC 1-813-696-6966 (Canada)		
Prepared By:	Cenovus Energy Inc. Health and Safety		
Phone Number:	1-403-766-2000		
Emergency Telephone:	1-877-458-8080, CANUTEC 1-813-696-6966 (Canada)		
2. COMPOSITION/INFORMATION ON INGREDIENTS			
Hazardous Ingredients	CAS Number	Approximate Concentration (%)	
Petroleum Crude Oil	8002-05-9	100 v/v	
Benzene	71-43-2	0.1 – 1.0 v/v	
Hydrogen Sulfide in liquid is <0.1% v/v; vapour phase may contain higher concentrations.			
3. HAZARDS IDENTIFICATION			
Routes of Entry:	Skin contact, skin absorption, eye contact, inhalation, ingestion		
Emergency Overview:	Warning: Flammable liquid and vapour. Liquid and vapour may cause irritation or burns to eyes, nose and throat. Inhalation of vapour may cause dizziness and drowsiness. Possible cancer hazard (benzene). Possible asphyxiation hazard (hydrogen sulfide). Wear personal protective equipment appropriate for the task.		
WHMIS R2, D2-A, D2-B NFPA 7-4, RD, 103	 		
Potential Health Effects:	Contains material which may cause cancer after long-term, repeated skin contact.		
4. FIRST AID MEASURES			
Eye Contact:	Immediately flush eyes with large amounts of lukewarm water for 15 minutes. Lift upper and lower lids at intervals. Seek medical attention if irritation persists.		
Skin Contact:	Remove contaminated clothing. Flush skin with water. Get medical attention if irritation persists or large area of contact. Decontaminate clothing before re-use.		
Inhalation:	Ensure own safety. Remove victim to fresh air. Give oxygen, artificial respiration, or CPR if needed. Seek medical attention immediately.		
Ingestion:	Give 2-3 glasses of milk or water to drink unless patient is unconscious or has a decreased level of alertness. DO NOT INDUCE VOMITING. Keep patient warm and at rest. Seek medical attention immediately.		

## Alberta Oil/Tar Sands

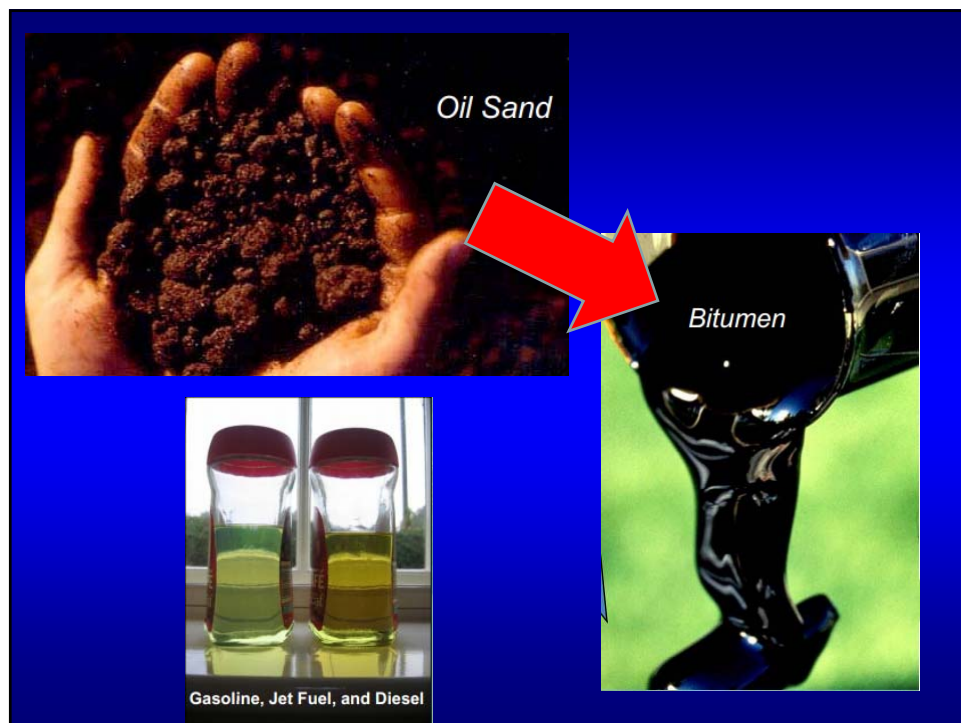




## Alberta Tar/Oil Sands

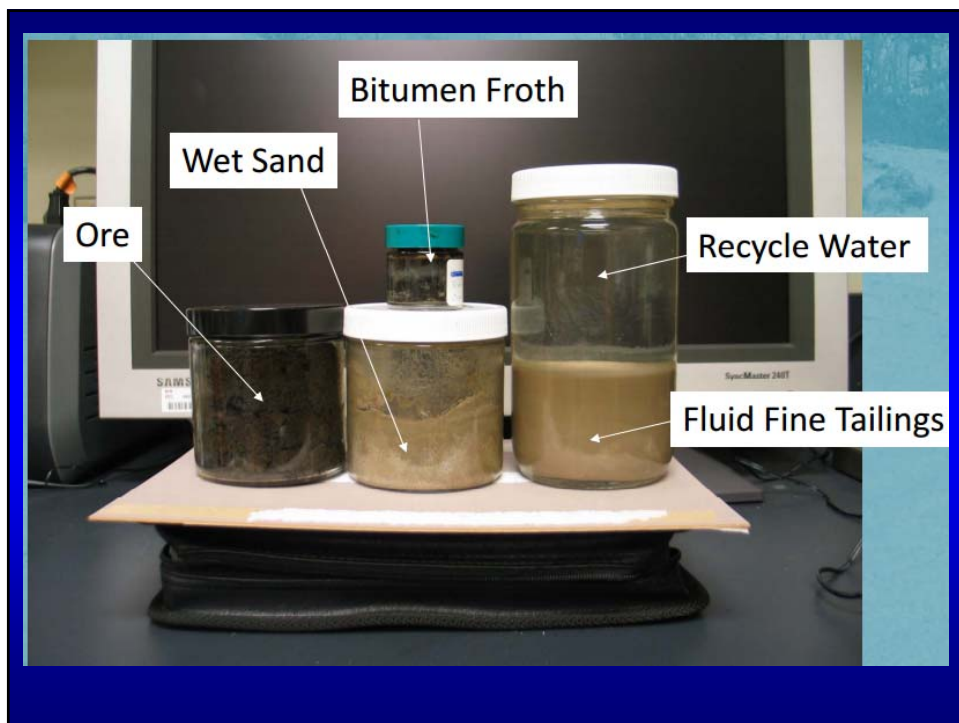
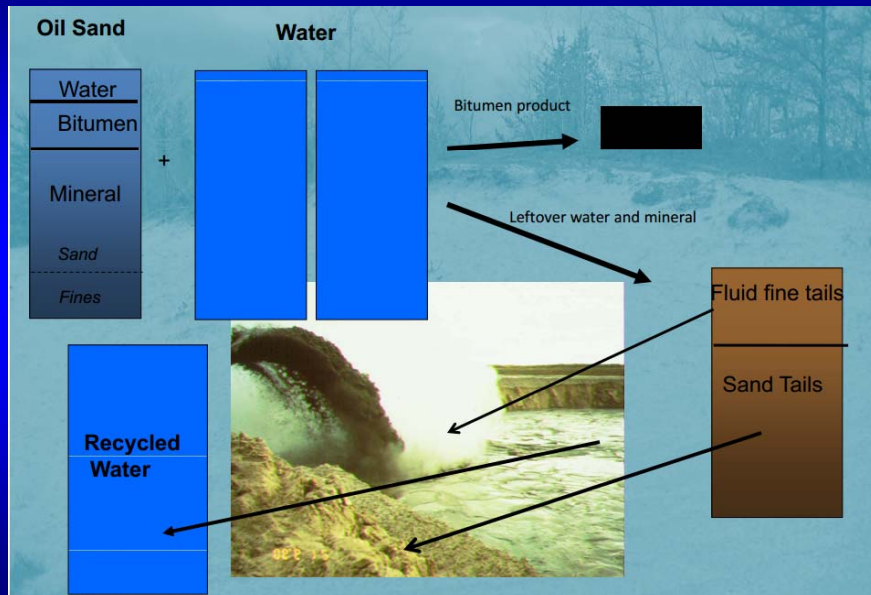
- “Typical Composition”
  - Mineral 85 %
  - **Bitumen 10% - “extra heavy crude”**
  - Water 5% (with soluble salts)

Crude	Maximum viscosity, mPa s	Gravities °API (S.G. = 141.5/(131.5-°API))
Light	1- 1000	20-40
Heavy	1000 - 10,000	10-20
Tars	10,000 –100,000	<10





## Bitumen Extraction

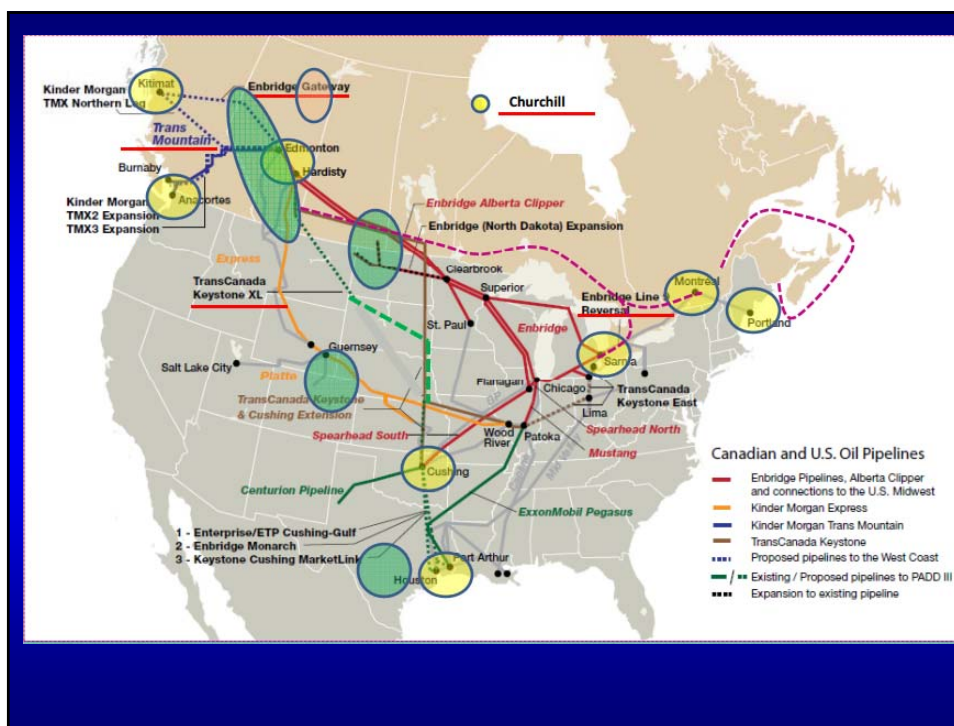


## Prep for transport

- Upgrade: Synthetic Crude = SynBit
  - Remove carbon, add hydrogen
- Dilute: Diluted Bitumen = Dilbit
  - Paraffinic (C6-C6 natural gas condensates)
  - Naptha or gas oils, conventional crudes
  - Can span a wide range of compositions

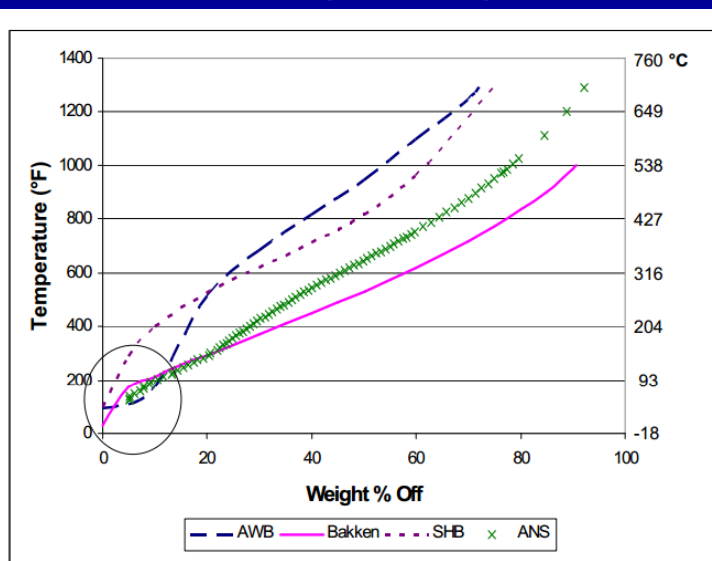
## Prep for transport

- Bitumen is “blended” with light oil to meet transmission pipeline specs
  - Needs 30% by volume of diluent for dilbit
  - Needs 50% by volume of synthetic crude for synbit
- Railcar/vessel specs vary





## Boiling Ranges



Access Western Blend Dilbit (AWB) Surmont Heavy Blend Synbit (SHB)  
Bakken and Alaskan North Slope (ANS) are included for comparison

	Benzene Content (%)
Dilbit	0.03 - 0.3
Synbit	<0.5
Bakken	0.1 - 1.0
ANS	0.3

## Spills

- If a spill of oil sands products were to occur, responders will have to prepare for both a light, floating oil depending on the diluent used and the potential for a heavy, submerged or sinking oil

## Major OSP spills

- 2007 – Burnaby BC pipeline spill
  - No air monitoring concerns
  - No submerged/sunken oil detected



## Major OSP Spills

- 2010 – Kalamazoo River
  - Air quality
    - Diluent had low flash point
    - 331 people reported adverse effects
  - Submerged and sunken oil issues

## Air Monitoring & Sampling

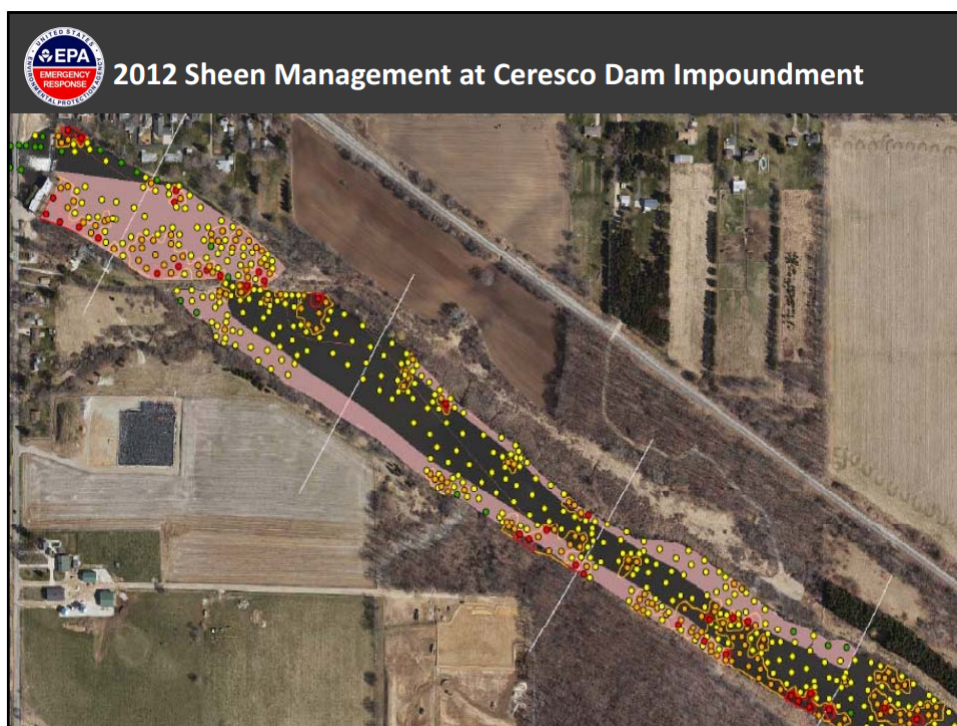


- Public Health concern for residents and workers during first 30 days
- Thousands of air monitoring readings collected
- Hundreds of air samples collected
- Voluntary evacuation at 60 residences

## Air Monitoring & Sampling



- Air monitoring conducted using:
  - MultiRAEs
  - Benzene UltraRAEs
  - AreaRAEs
  - Draeger tubes
  - HAPsites
- Air Sampling conducted using:
  - Summa Canisters Summa Canisters
  - Tedlar Bags – Mobile Lab
- Evacuation and Re-entry Decision Trees Established
- Benzene – main public health driver
- Evacuation Action Level –
  - 200 ppbv benzene when monitoring
  - 60 ppbv benzene when sampling
- Reoccupation Action Level – 6 ppbv benzene – sampling

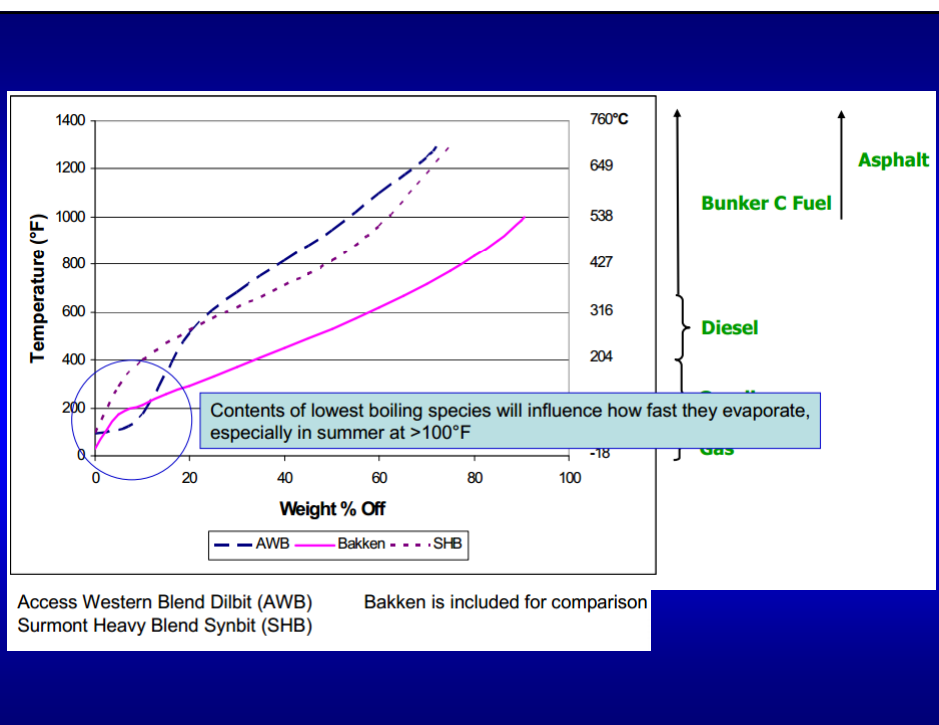


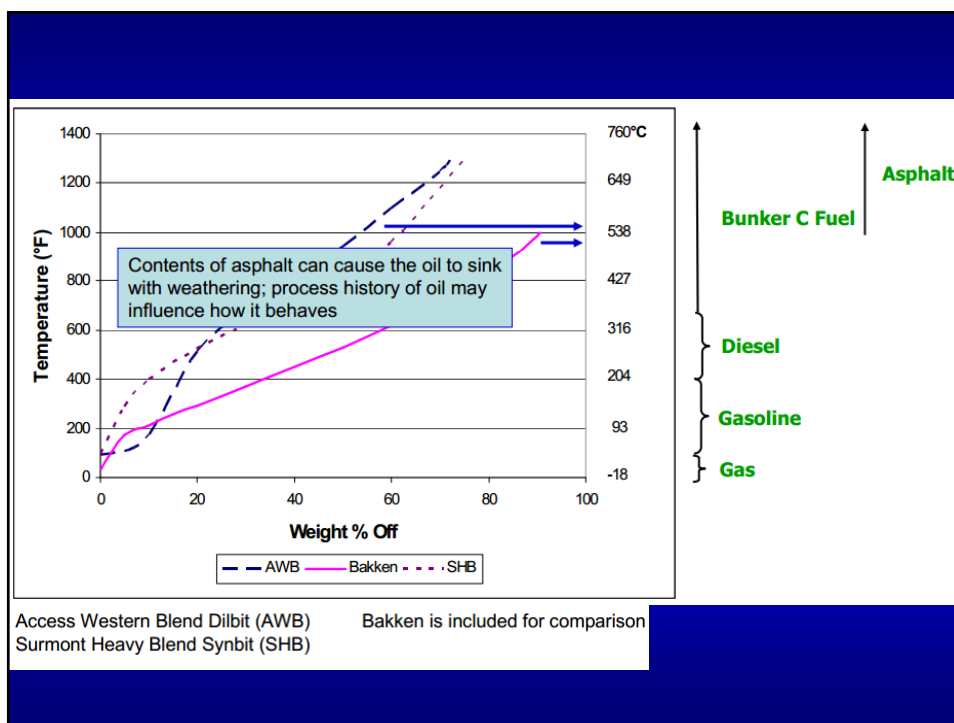




# OSP Response Considerations

- MSDS Availability
- Properties
  - Content of lowest boiling components that boil below 200 F
    - Air quality immediately after spill
    - Rate of loss
  - Contents of highest boiling components
    - Submerged and Sunken oil?





## Response Considerations

- Toxicity
- Tactics

